

Le8

34

"Aromatic Nitro compounds"

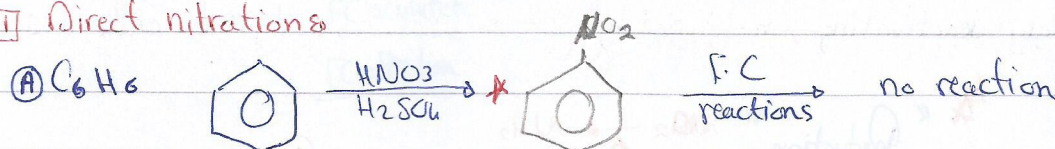
Nitrating agents

give NO_2^+ (nitronium ion)

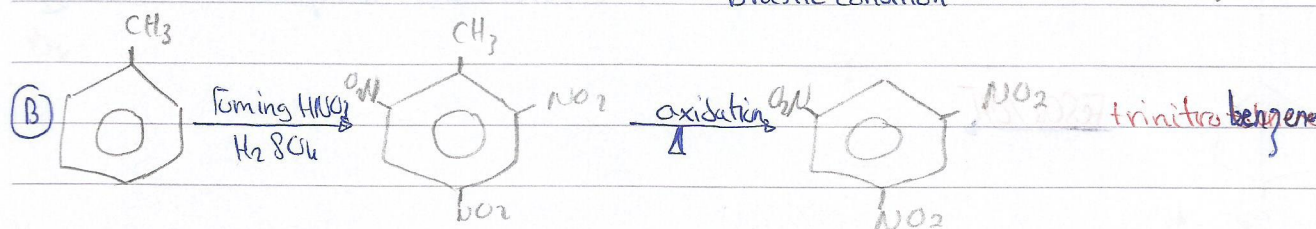
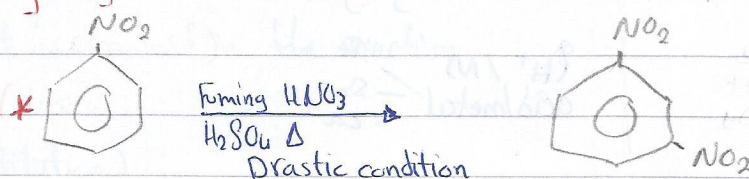
- 1] conc HNO_3 gives low concentration of NO_2^+
- 2] Fuming HNO_3 (6-12% NO_2 gas) $\rightarrow$ higher concentration of NO_2^+
- 3] Mixed acids ($\text{HNO}_3/\text{H}_2\text{SO}_4$) $\rightarrow$ most commonly used + good conc of NO_2^+
- 4] Acetyl nitrate ($\text{CH}_3\text{COONO}_2$) kn as non-acidic nitrating agent comes from (Ac anhydride / Fuming HNO_3)
- 5] Nitronium salts $\rightarrow$ ($\text{NO}_2^+ \text{ClO}_4^-$) nitronium perchlorate $\rightarrow$ nitration at room temperature

Synthesis

Direct nitrations

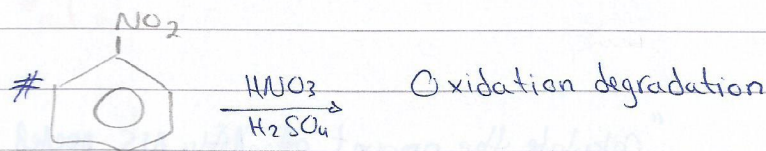
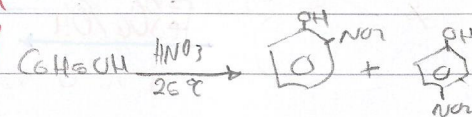


(NO_2 is deactivating by - Induction and - mesomerism)



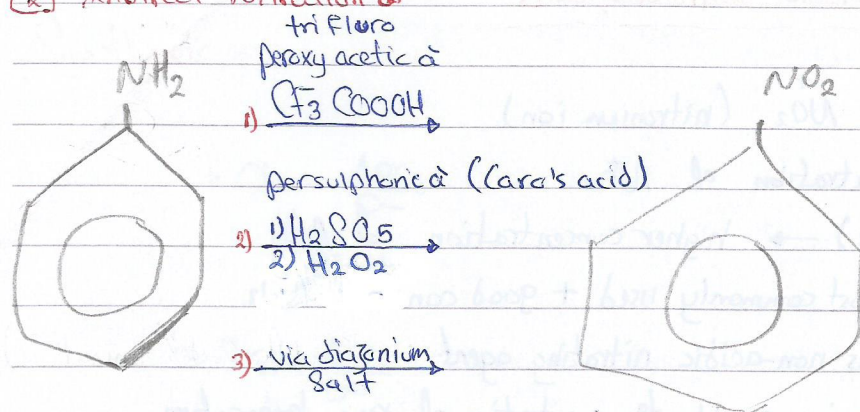
C) $\text{C}_6\text{H}_5\text{NH}_2$ (Aniline) colorless + highly reducing agent

D) $\text{C}_6\text{H}_5\text{OH}$ (Phenol) colorless + highly reducing agent



must apply protection by acetylation by CH_3COCl or $(\text{CH}_3\text{CO})_2\text{O}$

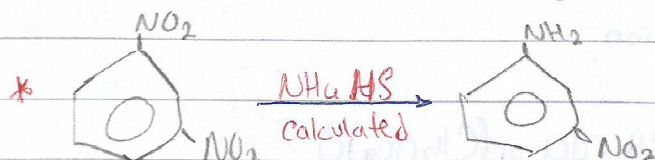
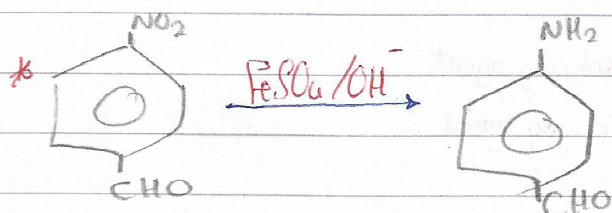
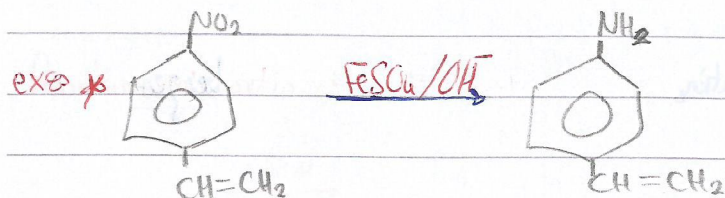
2 Indirect Nitration



Reactions

1 of NO_2 Strongly deactivating m-directory $\rightarrow$ reduction depends on the medium

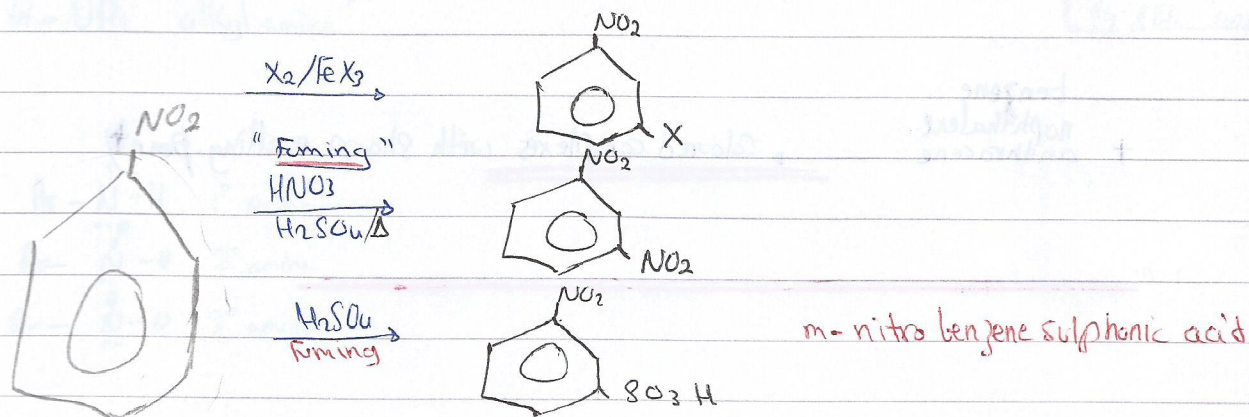
Reduction $NO_2 \rightarrow NH_2$			
1 Catalytic hydrogenation	2 Chemical hydrogenation	3 $FeSO_4/OH^-$	4 NH_4HS
$H_2 / Cat \leq \begin{matrix} Ni \\ Pt \\ Pd \end{matrix}$	$(H^+ / N) \leq \begin{matrix} Fe \\ Sn \\ Zn \end{matrix}$	(used if a reducing gp is present)	ammonium hydrogen sulphide (Selective)



"calculate the amount of NH_4HS needed to reduce one NO_2 "

12) reaction of the ring

A) Electrophilic aromatic substitution (EAS)



↓
less reactive

$\xrightarrow{FC\text{ acylation}}$
 $\xrightarrow{FC\text{ alkylation}}$

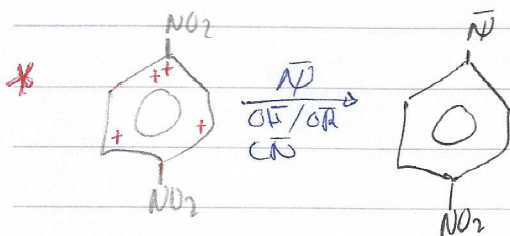
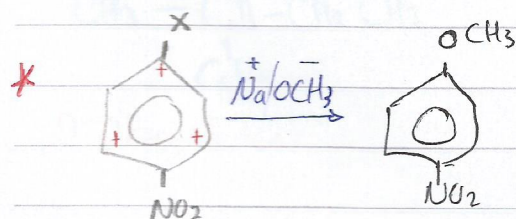
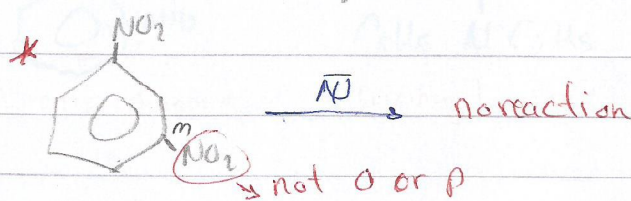
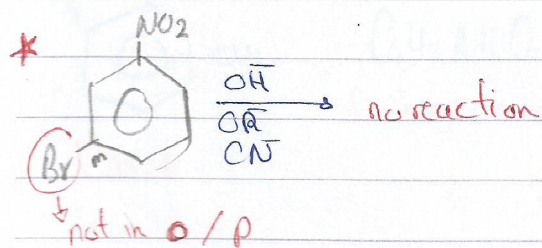
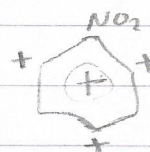
No reaction

* Nitro benzene is used in FC reactions and not benzene as a solvent?
 Because nitro benzene will not be involved in the reaction

B) NS (Nucleophilic Substitution)

* Nitro benzene is more reactive in NS than benzene?

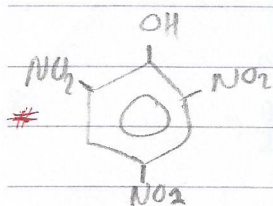
NO_2 pulls e^- and causes +ve charge in the ring



Ⓒ Molecular complex formation

poly nitro arenes

aromatic "arene" π system π π interaction π π interaction π π interaction
"polynuclear"



+ benzene or
naphthalene or
anthracene

→ Coloured complexes with sharp melting points

2,4,6-trinitro phenol